



Liquid chromatography–tandem mass spectrometry direct injection analysis of organophosphorus flame retardants in Ontario surface water and wastewater effluent



Chunyan Hao^{a,*}, Paul A. Helm^b, David Morse^a, Eric J. Reiner^a

^a Laboratory Services Branch, Ontario Ministry of the Environment and Climate Change, 125 Resources Road, Etobicoke, Ontario, M9P 3V6, Canada

^b Environmental Monitoring and Reporting Branch, Ontario Ministry of the Environment and Climate Change, 125 Resources Road, Etobicoke, Ontario, M9P 3V6, Canada

HIGHLIGHTS

- LC-MS/MS direct injection analysis method for determination of OPFRs in water.
- ACE C18 and ACE C18-PFP columns compared for isomer separation capacities.
- “trap” column used to eliminate background signal during LC-MS/MS analysis.
- Analyte stability studies performed in real water samples.
- Seven OPFRs detected in Ontario surface water and eight detected in waste water.

ARTICLE INFO

Article history:

Received 20 July 2017

Received in revised form

8 October 2017

Accepted 9 October 2017

Available online 10 October 2017

Handling Editor: Myrto Petreas

Keywords:

Organophosphorus flame retardants (OPFRs)

Direct injection analysis (DIA)

Liquid chromatography–tandem mass spectrometry (LC-MS/MS)

Water analysis

ABSTRACT

Organophosphorus flame retardants (OPFRs) started to be used in plastics, electronics and furnishings back in the 1960s and became popular again last decade. They are now widely present in the environment and regarded as “new” emerging organic pollutants. An effective liquid chromatography–tandem mass spectrometry (LC-MS/MS) direct injection analysis (DIA) method was developed to monitor OPFR levels in aquatic environment. The removal of sample extraction and concentration steps not only improved operation efficiency, but also reduced the potential contamination commonly observed during the sample preparation process before. Positive background signals from the analytical instrument were eliminated by employing a “trap” column in front of the sample injector while an ACE C18 and an ACE C18-PFP column were compared for the separation of OPFRs. Nineteen OPFR related compounds were evaluated and rapid signal drops were observed for seven of them including TOTP, TMTP, TPTP, TEHP, T35DMPP, T2iPPP and EHDP, due to their low water solubility. The other twelve compounds, TMP, TEP, TPrP, TiPP, TBP, TCEP, TCPP, TDCPP, TPP, TBEP, BDCP and BEHP, were included for the measurement of OPFRs in drinking water, surface water, ground water and wastewater effluent samples. The instrumental detection limits of these twelve OPFRs at signal-to-noise ≥ 3 were in the 1.5–30 ng/L range. The method was applied for the determination of OPFRs in surface water and wastewater samples in Ontario, Canada, and BEHP, TBEP, TBP, TCEP, TCPP, TDCPP, and TEP were commonly detected.

Crown Copyright © 2017 Published by Elsevier Ltd. All rights reserved.

1. Introduction

Flame retardants are chemicals that have been added in various consumer products such as building materials, electronics, furnishings, motor vehicles, airplanes, plastics, polyurethane foams,

and textiles to prevent the spread of fire by inhibiting, suppressing or delaying the production of flames. Their usage continuously increases maybe to a total of 5.7 billion pounds in 2019 due to rising safety standards worldwide (Anon 1, 1622). Because of their persistence, bioaccumulation and toxicity, many halogenated substances and flame retardants, such as polychlorinated biphenyls (PCB), perfluorooctane sulfonic acid (PFOS), tetra- to heptabromodiphenyl ethers, and hexabromocyclododecane (HBCD), are defined

* Corresponding author.

E-mail address: chunyan.hao@ontario.ca (C. Hao).

as persistent organic pollutants (POPs) (Anon 2) by the Stockholm Convention and have been banned from further usage. Organophosphate esters, mainly triesters (trialkyl, trichloroalkyl and triaryl esters of phosphoric acid), were used as flame retardants and plasticizers during the 60s and 70s, but replaced by newer generation of flame retardants due to the significant residue levels detected in the environment. These chemicals returned to the market as suitable alternatives after the European Union banned the usage of certain polybrominated diphenyl ether (PBDE) flame retardants in 2004 (European Flame Retardants Association). Organophosphate ester flame retardants consist of a diverse class of chemicals with aromatic, halogens and other function groups in the molecules which can enable a wide variety of applications in different fields. They are usually physically mixed in as additives and not chemically bonded to the materials, therefore, very likely to evaporate or leach from the commercial products and release into the environment. OPFRs have been listed as high-production-volume chemicals and are believed to be present in the environment ubiquitously, from wastewater (Rodil et al., 2005; Meyer and Bester, 2004), air (Marklund et al., 2005), sludge (Zeng et al., 2014), soil/sediment (Cao et al., 2012) to household dust (Fan et al., 2014), surface water (Andresen et al., 2004; Bollmann et al., 2012; Martínez-Carballo et al., 2007; Kim et al., 2010), ground water (Fries and Püttman, 2003), drinking water (Bacaloni et al., 2007), etc. They have also been recognized as a major type of emerging organic pollutants recently due to their potential toxic effects (van der Veen and de Boer, 2012; Reemtsma et al., 2008; Wei et al., 2015). Studies showed that OPFRs could be linked to health problems, for example, TBP might be related to sick house syndrome, TPP and TBP were neurotoxic, TCEP, TDCCP, TCPP and TBEP were carcinogenic, TPP and TDCPP were associated with hormone disturbance and a decline of semen quality (Andresen et al., 2004; Bacaloni et al., 2007).

Gas chromatography (Toda et al., 2004; LeBel et al., 1981; Fries and Püttman, 2001) coupled with mass spectrometry (GC-MS) and nitrogen-phosphorous detector (GC-NPD) were employed commonly in the past for the measurement of OPFRs in environmental samples, with an escalating number of liquid chromatography-tandem mass spectrometry (LC-MS/MS) based methods (Dirtu et al., 2012; Santín et al., 2016; Kosarac et al., 2016) emerged in the last decade. Interferences can be a concern for GC based method since electron impact ionization mass spectra of some OPFRs lack structural information (Ma and Hites, 2013), and other phosphorus-containing compounds in the sample matrices might cause false positive or biased-high results when co-eluting with target analytes using NPD. Soft chemical ionization in positive ion MS mode was reported to be able to provide enhanced selectivity for identification with pseudo molecular ions $[M+H]^+$ produced in GC-based analyses (Bergh et al., 2010). The same advantage also applies to the soft electrospray ionization (ESI) in LC-MS/MS technology. More specificity could be achieved by tandem mass spectrometry using multiply reaction monitoring (MRM) with the pair of a pseudo molecular ion and a fragment ion generated by collision-induced dissociation. LC-MS/MS technology is also suitable for the determination of mono- and di-esters of phosphoric acid (Reemtsma et al., 2011; Hoffman et al., 2015), which are not volatile enough for GC analysis. These mono- and di-esters were either produced as industrial chemicals such as di(2-ethylhexyl) phosphoric acid (DEHP) and mono(2-ethylhexyl) phosphoric acid (MEHP), or were metabolized/hydrolyzed from triesters of phosphoric acid (Reemtsma et al., 2011).

OPFRs have been extensively studied in Europe and Asia, while very limited environmental monitoring data were reported in Canada (LeBel et al., 1981; Andresen et al., 2007). Certain organic flame retardant substances including several OPFRs are being

assessed under the Chemical Management Plan by Environment and Climate Change Canada. More detailed environmental monitoring and sources determination information is needed to support this assessment. Aqueous phase is a key medium for the transportation of the OPFRs in the environment. Although we didn't find previous publications to report human health are directly impacted by these chemicals through drinking water, the concentrations of OPFRs in drinking water is certainly associated with health concerns. Surface water and ground water play important roles for the ecosystem and are commonly used as source water for drinking water, while wastewater discharge was identified as a potential source for the OPFRs to enter the environment (Reemtsma et al., 2008). It is very important to monitor the levels of OPFRs in these environmental water samples for both wild life and human health.

The biggest challenge in OPFR analysis is the background contamination as indicated by the first worldwide inter-laboratory study (Brandtsma et al., 2013). Target analytes may leach from plastic containers/labwares during sample transportation, storage, enrichment and analysis. Background may also come from impurities in solvents and chemical reagents used. Previously published OPFR measurement methods for environmental water samples normally engaged a sample preparation procedure like liquid-liquid extraction (Andresen et al., 2004, 2007; Martínez-Carballo et al., 2007; García-López et al., 2007) or solid-phase extraction (Rodil et al., 2005; Bollmann et al., 2012; Kim et al., 2010; Bacaloni et al., 2007; Wang et al., 2011; Li et al., 2014) to extract and concentrate the target analytes. After a contraction factor of 100–2000, the limits of quantitation in previous LC-MS/MS methods for water analysis are in the range of 0.3–2900 ng/L with either one or two MRM transition(s). Not only is the sample preparation procedure time-consuming and labor intensive, it also expands likelihood for background contamination. The current study intended to develop a LC-ESI-MS/MS method to determine as many OPFRs as possible in aqueous environmental matrices by direct injection analysis that can offer comparable detection limits as previously published methods. Nineteen OPFR related compounds have been evaluated and twelve were included in this method: TMP, TEP, TPrP, TiPP, TBP, TCEP, TCPP, TDCPP, TPP, TBEP plus two diester metabolites BDCP (a metabolite of TDCPP) and BEHP (a metabolite of TEHP). The other seven OPFRs, TOTP, TMTP, TPPT, TEHP, T35DMPP, T2iPPP and EHDP were excluded due to stability issues during a sample storage study. The developed method is able to analyze 12 OPFR related compounds in less than 20 min and it has been applied to support Ontario's surface water monitoring survey and the contamination source investigation.

2. Experimental

2.1. Chemicals & reagents

Stock solutions of tri-methyl phosphate (TMP), tri-iso-propyl phosphate (TiPP) and bis(2-ethylhexyl) phosphate (BEHP) were prepared from the corresponding neat standards purchased from Sigma-Aldrich (Oakville, ON, Canada). Individual custom-made stock solutions of other native OPFRs, tri-*o*-tolyl-phosphate (TOTP), tri-*m*-tolyl-phosphate (TMTP), tri-*p*-tolyl-phosphate (TPPT), Tris (2-ethylhexyl) phosphate (TEHP), tris (3,5-dimethylphenyl) phosphate (T35DMPP), tris (2-isopropylphenyl) phosphate (T2iPPP), 2-ethylhexyl diphenyl phosphate (EHDP), tri-ethyl phosphate (TEP), tri-*n*-propyl phosphate (TPrP), tri-*n*-butyl phosphate (TBP), tris(2-chloroethyl) phosphate (TCEP), tris(1,3-dichloro-2-propyl) phosphate (TDCPP), triphenyl phosphate (TPP), tris(2-butoxyethyl) phosphate (TBEP), and bis(1,3-dichloro-2-propyl) phosphate (BDCP) and isotope-labelled OPFRs were purchased from

Download English Version:

<https://daneshyari.com/en/article/5745713>

Download Persian Version:

<https://daneshyari.com/article/5745713>

[Daneshyari.com](https://daneshyari.com)